$C_{12}H_{14}O_3$

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1-Benzyl-5-methoxycarbonylmethylthio-4-nitroimidazole

HAYTHEM SAADEH, CHARLES M. THOMPSON, ELIAS FERNANDEZ AND STEPHEN F. PAVKOVIC

Department of Chemistry, Loyola University of Chicago, 6525 N. Sheridan Road, Chicago, IL 60626-5385, USA

Abstract

Molecules of the title compound, methyl 1-benzyl-4-nitro-5-imidazolylthioacetate, $C_{13}H_{13}N_3O_4S$, can be viewed as an arrangement of three intersecting planes of atoms. The plane of the imidazole ring and its bonded atoms (r.m.s.d. = 0.030 Å) intersects the plane of the benzyl group (r.m.s.d. = 0.004 Å) at an angle of 89.0 (5)°. The plane of atoms extending from the S atom to the methyl group (r.m.s.d. = 0.004 Å) intersects the first two planes at angles of 85.9 (5) and 15.2 (5)°, respectively. The imidazole ring is twisted about the S—C3(ring) bond so that the C11—S—C3—N1(ring) torsion angle is obtuse. The conformation of the chain of atoms from the imidazole ring to the benzyl group is nominally *trans*, while that to the thioacetate is *gauche*.

Comment

The thioether-substituted nitroimidazole, (I), was intended to be a precursor, which should react *via* a cyclization pathway similar to that of a comparably substituted benzenoid compound (Sicker, Reifegerste, Hauptmann, Wilde & Mann, 1985), leading to a sulfur-containing purine analog. However, all attempts to cyclize (I) failed and its regiochemistry was in doubt, *i.e.* it was not known whether the S substituent was at the C1 or C3 position. Proton NMR chemical-shift differences between the C1 and C3 substituent patterns were insufficient for assignment, and convergent synthetic routes did not confirm a regioisomer. A diffraction study of crystals of (I) was thus undertaken and showed the molecule

to contain a benzyl group attached to the imidazole ring at position N1, a nitro group at C2 and a thio group at C3.

(I)
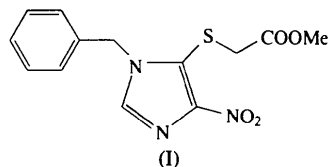
Details of the structure can be described in terms of three intersecting planes. A central plane composed of ten atoms (r.m.s.d. = 0.030 Å) contains the imidazole ring, nitro group and C4 and S atoms. A second plane contains the seven atoms of the benzyl group (r.m.s.d. = 0.004 Å) and intersects the central plane at an angle of 89.0 (5)°. The torsion angle involving atoms common to these two planes, C5—C4—N1—C3, is 102.7 (4)°. The third plane consists of six atoms and contains the S atom and the chain of atoms bonded to it (r.m.s.d. = 0.004 Å). It intersects the central plane at an angle of 85.9 (5)°. The C11—S—C3—N1 torsion angle is 117.4 (4)°. The benzyl and thio group planes intersect at an angle of 15.2 (5)°.

The benzyl and thio groups bonded to the imidazole ring have different conformations. Whereas the C10—C5 bond of the benzyl group is nominally *trans* to the C4—N1 bond [torsion angle 151.2 (4)°], the C12—C11 bond is *gauche* relative to the S—C3 bond [torsion angle −72.1 (4)°]. This molecular arrangement at the S atom results in closest and marginally favorable non-bonded distances from O1 to a C11 H atom [2.36 (1) Å], and from O4 to a C4 H atom [2.83 (1) Å].

Three related compounds have been reported that have the same arrangement of ten atoms as is present in the central plane of (I). All contain a methyl group bonded to the imidazole ring at position N1, a nitro group at C2 and a substituted S at C3. One compound contains a purine group at the S atom (Cook & Bugg, 1975), the second a hydroxypyridine group (Puig-Torres, Martin, Larson & Simonsen, 1984) and the third a triazole ring (Dupont, Dideberg & Jamoulle, 1984).

Only minor geometrical differences are noted among the ten atoms common to all four compounds. However, two features present in structure (I) distinguish it from the other three. Firstly, the twist of the imidazole ring around the S—C3 bond in (I) results in a C11—S—C3—N1 torsion angle that is obtuse. In the three related structures, the ring is twisted in the opposite manner so that the comparable chains of atoms have an acute torsion angle. A change to this arrangement in structure (I) would move C4 too close to O4 and lead to steric destabilization. Secondly, the *gauche* conformation noted for the C12—C11—S—C3 linkage in structure (I) is *trans* for comparable linkages in all of the related structures. A change to this arrangement in (I) would eliminate the intramolecular, and presumably favorable, non-bonded contacts to atoms O1 and O4.
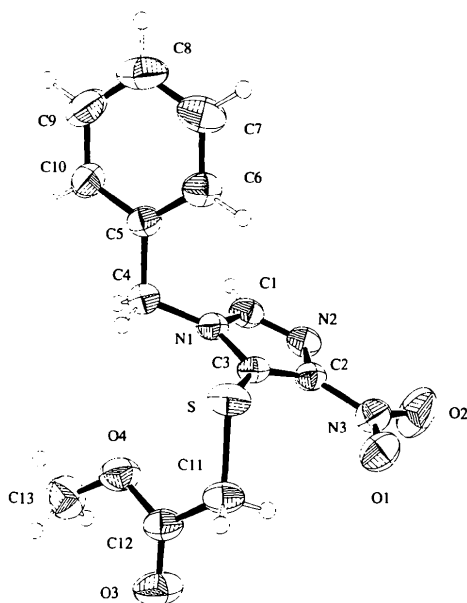
Fig. 1. An *ORTEP*II diagram (Johnson, 1976) of the title molecule showing 50% probability ellipsoids. H atoms are shown as small spheres of arbitrary radii.

Experimental

The title compound (I) was prepared by H. Saadeh from the parent carboxylic acid (Iddon, Khan & Lim, 1987). Suitable crystals for diffraction studies were obtained by evaporation of an ethyl acetate solution.

Crystal data

$C_{13}H_{13}N_3O_4S$
$M_r = 307.33$
Triclinic
$P\bar{1}$
$a = 9.4675 (12)$ Å
$b = 10.1833 (13)$ Å
$c = 8.2964 (10)$ Å
$\alpha = 112.383 (4)°$
$\beta = 106.408 (5)°$
$\gamma = 91.788 (4)°$
$V = 700.7 (1)$ Å^3
$Z = 2$
$D_x = 1.46$ Mg m^{-3}
$D_m = 1.43 (2)$ Mg m^{-3}
D_m measured by flotation in mixed organic solvents

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 35 reflections
$\theta = 12.2–15°$
$\mu = 0.24$ mm^{-1}
$T = 294$ K
Prismatic
$0.30 \times 0.30 \times 0.22$ mm
Pale yellow

Data collection

Modified Picker FACS-I diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical *via* φ scans with χ at 90°
$T_{min} = 0.93$, $T_{max} = 0.95$
2960 measured reflections
2903 independent reflections
2325 observed reflections
[$F > 3\sigma(F)$]

$R_{int} = 0.027$
$\theta_{max} = 26.5°$
$h = 0 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -9 \rightarrow 10$
4 standard reflections monitored every 200 reflections intensity decay: 2%

Refinement

Refinement on F
$R = 0.040$
$wR = 0.047$
$S = 1.175$
2325 reflections
191 parameters
H-atom parameters not refined
$w = 0.8834/[\sigma^2(F) + 0.000143F^2]$

$(\Delta/\sigma)_{max} = 0.015$
$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = -0.12$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B).

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S	0.13138 (5)	0.86958 (4)	0.41478 (6)	0.0443 (2)
O1	-0.2122 (2)	0.7898 (2)	0.2084 (2)	0.057 (1)
O2	-0.3635 (2)	0.6771 (3)	0.2810 (3)	0.086 (1)
O3	0.1649 (2)	0.5443 (2)	-0.0209 (2)	0.066 (1)
O4	0.2651 (2)	0.6069 (2)	0.2801 (2)	0.057 (1)
N1	0.1007 (1)	0.7183 (1)	0.6163 (2)	0.037 (1)
N2	-0.1406 (2)	0.6376 (2)	0.5326 (2)	0.043 (1)
N3	-0.2385 (2)	0.7261 (2)	0.2989 (2)	0.048 (1)
C1	-0.0077 (2)	0.6461 (2)	0.6417 (2)	0.042 (1)
C2	-0.1159 (2)	0.7102 (2)	0.4335 (2)	0.037 (1)
C3	0.0324 (2)	0.7629 (2)	0.4803 (2)	0.034 (1)
C4	0.2587 (2)	0.7454 (2)	0.7211 (3)	0.045 (1)
C5	0.2949 (2)	0.8618 (2)	0.9131 (2)	0.037 (1)
C6	0.2128 (2)	0.9726 (2)	0.9522 (3)	0.047 (1)
C7	0.2487 (3)	1.0783 (2)	1.1292 (3)	0.060 (1)
C8	0.3677 (3)	1.0737 (3)	1.2653 (3)	0.067 (1)
C9	0.4500 (3)	0.9643 (3)	1.2279 (3)	0.065 (1)
C10	0.4140 (2)	0.8582 (3)	1.0520 (3)	0.050 (1)
C11	0.1034 (2)	0.7524 (2)	0.1787 (2)	0.044 (1)
C12	0.1812 (2)	0.6241 (2)	0.1354 (2)	0.042 (1)
C13	0.3433 (3)	0.4847 (3)	0.2461 (4)	0.067 (1)

Table 2. *Selected geometric parameters* (Å, °)

S—C3	1.740 (1)	N1—C3	1.377 (2)
S—C11	1.799 (2)	N1—C4	1.458 (2)
O1—N3	1.230 (2)	N2—C1	1.304 (2)
O2—N3	1.216 (2)	N2—C2	1.355 (2)
O3—C12	1.201 (2)	N3—C2	1.427 (2)
O4—C12	1.316 (2)	C2—C3	1.378 (2)
O4—C13	1.444 (3)	C4—C5	1.512 (3)
N1—C1	1.352 (2)	C11—C12	1.494 (3)
C3—S—C11	101.1 (1)	N3—C2—C3	127.2 (1)
C12—O4—C13	117.0 (2)	S—C3—N1	122.1 (1)
C1—N1—C3	107.2 (1)	S—C3—C2	134.8 (1)
C1—N1—C4	124.9 (1)	N1—C3—C2	103.0 (1)
C3—N1—C4	127.9 (1)	N1—C4—C5	112.6 (1)
C1—N2—C2	103.5 (1)	C4—C5—C6	121.6 (2)
O1—N3—O2	123.5 (2)	C4—C5—C10	119.3 (2)
O1—N3—C2	118.3 (2)	C6—C5—C10	119.1 (2)
O2—N3—C2	118.2 (2)	S—C11—C12	119.6 (1)
N1—C1—N2	113.3 (1)	O3—C12—O4	124.3 (2)
N2—C2—N3	119.8 (1)	O3—C12—C11	121.0 (2)
N2—C2—C3	113.0 (1)	O4—C12—C11	114.7 (1)

All H atoms were found in subsequent Fourier electron-density difference maps. During refinement, H atoms were fixed in positions of idealized geometry (C—H = 0.95 Å) with U(H) = 0.08 Å^2 for methyl-group H atoms and U(H) = 0.06 Å^2 for the remaining H atoms.

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1152). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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endo-3,3-Diphenyltricyclo[3.2.1.0²·⁴]oct-6-ene

Mehboob Peeran

Department of Chemistry, St. Joseph's College, Bangalore, India 560 001

James W. Wilt,† Eugene J. Zaluzec and Stephen F. Pavkovic

Department of Chemistry, Loyola University of Chicago, 6525 N. Sheridan Road, Chicago, IL 60626-5385, USA
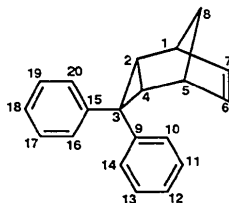
Abstract

The main feature in the title compound, $C_{20}H_{18}$, is the system of fused three-, five- and six-membered rings. The two phenyl substituents are bonded to one C atom of the three-membered ring and that ring adopts an *endo* conformation relative to the larger rings. This results in a phenyl-group atom being close to the diene bond in the fused rings. The contact distances are 2.912 (4) and 2.952 (3) Å. The plane of this phenyl group is nearly parallel to the diene bond. Planes of the two phenyl rings make an angle of 76.1 (2)°.

† Deceased May 13 1987.

Comment

The compound is one of two test molecules being used in an ongoing study of reactions involving Long Range Aryl Migration with Electrocyclic Ring Opening (LRAMERO) (Wilt & Tufano, 1985). In particular, the *endo* compound has been used as a vehicle for probing aryl-π-participation in addition and solvolysis reactions (Peeran, Wilt, Subramanian & Crumrine, 1989, 1993). In order to elucidate the mechanism of these reactions it became important to establish intramolecular contact distances for *exo* and *endo* conformations. This paper reports the structure of the *endo* conformer.

The main feature in this structure is the system of fused three-, five- and six-membered rings. The three-membered ring contains two phenyl substituents at methylene C3. The *endo* conformation places C3 *anti* to C8 and at a contact distance of 3.419 (3) Å. Correspondingly, there are shorter contact distances from C3 to the double-bonded atoms C6 and C7 of 2.957 (3) and 2.980 (3) Å, respectively. The phenyl groups are bonded to C3 at C9 and C15, and short contact distances C9···C6 and C9···C7 of 2.912 (4) and 2.952 (3) Å are noted. The C9–C14 phenyl group is nearly planar to the double bond as evidenced by comparable contact distances of 3.251 (4) for C10···C7 and 3.146 (4) Å for C14···C6, and by a small angle of 3.0 (4)° between the C6–C7 vector and plane of the phenyl group. The angle between this vector and plane of the second phenyl group (C15–C20) is 7.0 (5)°. The planes of the two phenyl groups intersect at an angle of 76.1 (2)°. All bond lengths and angles within the phenyl groups are normal with average geometric parameters of 1.381 (11) Å and 120.0 (9)°.
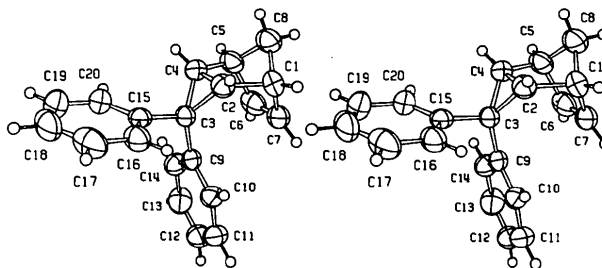

Fig. 1. An *ORTEP* (Johnson, 1976) stereoview of the molecule using displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radius.